Lecture Note #2 (Spring, 2022)

Cell potential and thermodynamics

1. Potentials
2. Cell potential
3. Standard potentials
4. Nernst equation
5. Pourbaix diagrams
6. Working electrode
7. Reference electrodes
8. Potential vs. energy

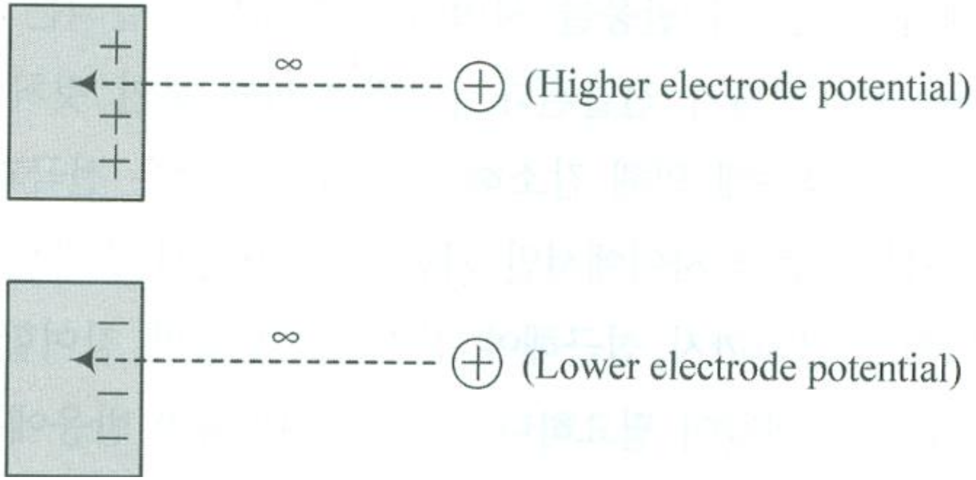
Fuller & Harb (textbook), ch.2, Bard (ref.), ch.1,2, Oh (ref.), ch.2

Potentials

Chemical potential, electrochemical potential,
electrical potential (**전위**), electrode potential

Electrical potential: The energy required to bring a positive charge of unit size to any phase (relative value)

Physics: positive charge. Electrochemistry: negative charge(electron)

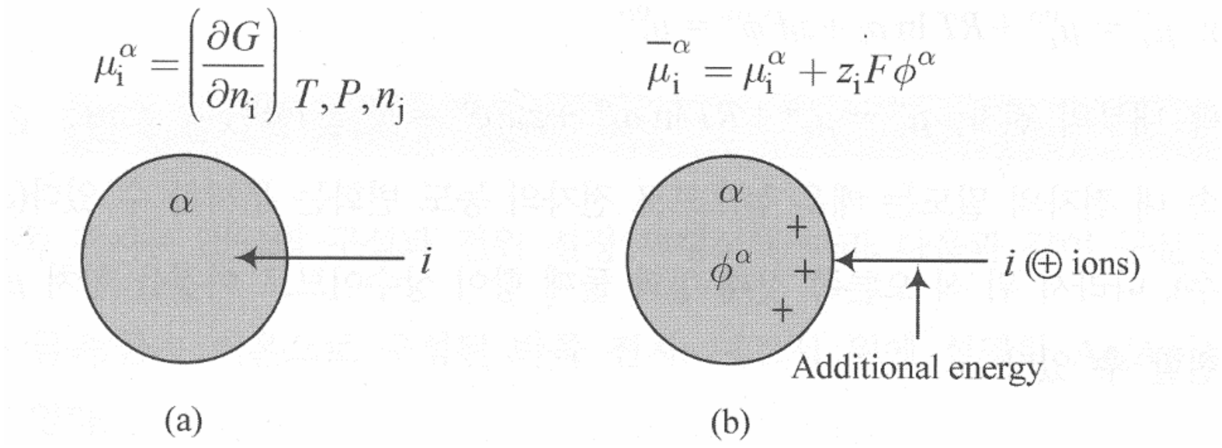


Oh, Fig. 1-2

Chemical potential vs. electrochemical potential

Chemical potential (화학전위): Changes in free energy required when adding compound i unit equivalents to any phase (α) under constant temperature and pressure→ reaction progress towards reduced chemical potential

Electrochemical potential(전기화학 전위): Substances with charges (electrons, ions) participate in the reaction. α If the potential is φ^α, when species i with the charge of the unit equivalent is added, not only the free energy change (μ_i^α) due to the concentration change, but also the change in electrical work (or energy), $z_iF\varphi^\alpha$, z_i is the charge of i, F is a faraday constant) occurs

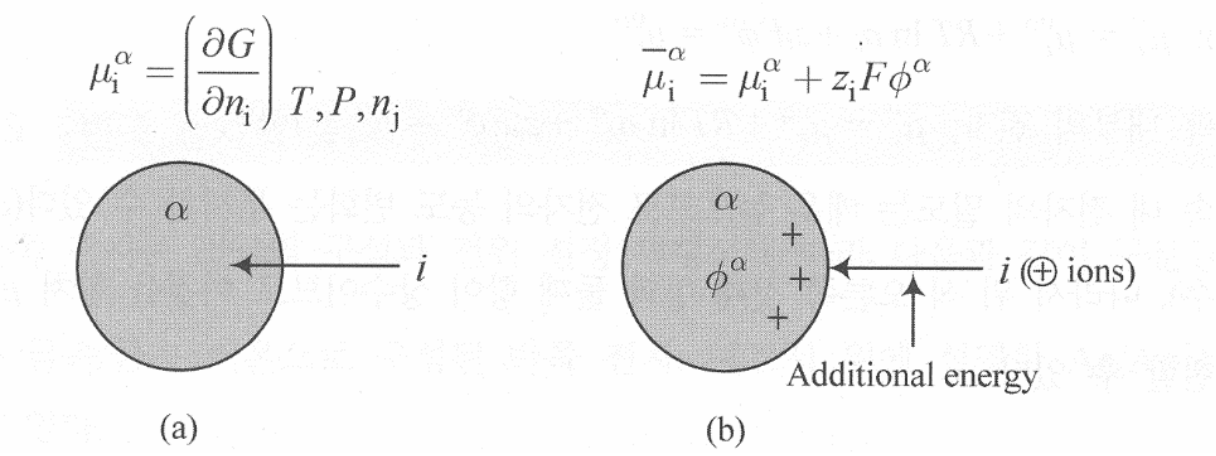


Oh, Fig. 2-2

Chemical potential vs. electrochemical potential

Chemical potential (화학전위): 온도와 압력이 일정한 조건에서 어떤 상(α)에 단위 당량의 화합물 i를 추가할 때 필요한 자유에너지의 변화 → 화학전위가 감소하는 방향으로 반응 진행

Electrochemical potential(전기화학 전위): 전하를 가진 물질(전자, 이온)이 반응에 참여. α 상의 전위가 φ^{α}라면 단위 당량의 전하를 가진 물질 i를 첨가할 때 농도 변화에 따른 자유에너지 변화(μ_i^{α})뿐 만 아니라 전기적 일(또는 에너지, $z_i F\varphi^{\alpha}$, z_i는 전하체 i의 전하, F는 패러데이 상수)의 변화도 발생



$$\mu_i^{\alpha} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

$$\bar{\mu}_i^{\alpha} = \mu_i^{\alpha} + z_i F\phi^{\alpha}$$

Oh, Fig. 2-2

Cell potential(셀 전위): thermodynamic

Why is it that chemical reactions in electrochemical cells proceed spontaneously in one direction and furnish current?
(thermodynamics: equilibrium, kinetics: reaction rate)
:
Cell potential of an electrochemical cell

$$E_{cell} = E_{cathode} - E_{anode}$$

Gibbs free energy, **$\Delta G = -nFE_{cell}$**

$\Delta G < 0 \rightarrow$ spontaneous

E_{cell}^0: standard potential = $E_{cathode}^0 - E_{anode}^0$

표준전위

$E_{cathode}^0$, E_{anode}^0: standard electrode potential of half reactions expresses as reductions vs. NHE(normal hydrogen electrode)

Textbook: $\Delta G = -W_{el}$ (electrical work), $W_{el} = nFU$, $U = E_{cell}$

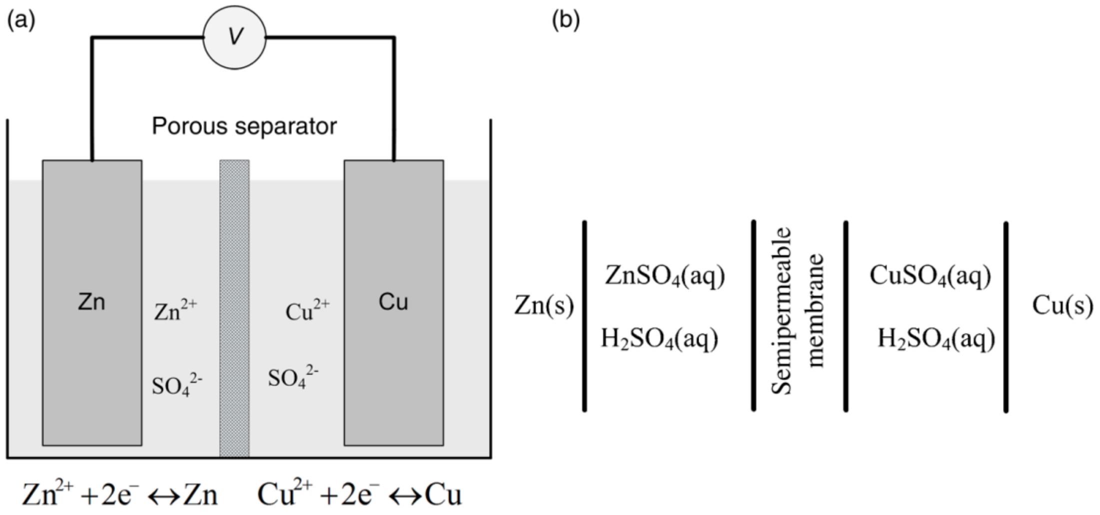


Figure 2.1 Daniel cell. (a) The physical representation. (b) Representation of the cell for thermodynamic analysis.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Cell: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$

- Right: $Cu^{2+} + 2e^- \rightarrow Cu$ $E^0 = +0.34$ V
- Left: $Zn^{2+} + 2e^- \rightarrow Zn$ $E^0 = -0.76$ V

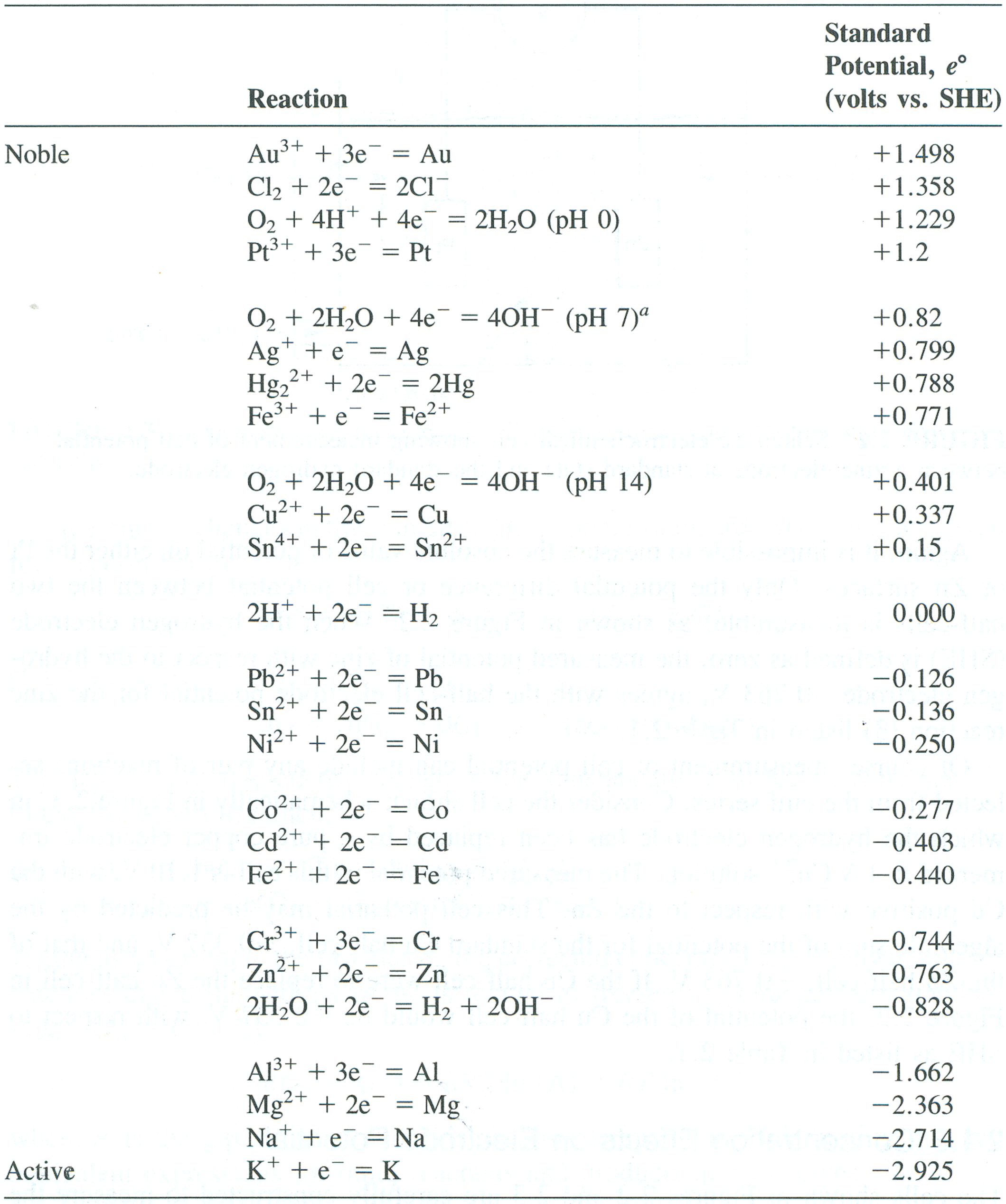
$$\mathbf{E_{cell}^0 = +0.34 - (-0.76) = +1.10\ V}$$

$\Delta G^0 = -2 \times 1.10(V) \times 96{,}485\ (JV^{-1}mol^{-1}) = -212\ kJmol^{-1}$

reaction → spontaneous

Standard electrode potential (표준전극전위)

E^0



	Reaction	Standard Potential, e° (volts vs. SHE)
Noble	$Au^{3+} + 3e^- = Au$	+1.498
	$Cl_2 + 2e^- = 2Cl^-$	+1.358
	$O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0)	+1.229
	$Pt^{3+} + 3e^- = Pt$	+1.2
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 7)[a]	+0.82
	$Ag^+ + e^- = Ag$	+0.799
	$Hg_2^{2+} + 2e^- = 2Hg$	+0.788
	$Fe^{3+} + e^- = Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 14)	+0.401
	$Cu^{2+} + 2e^- = Cu$	+0.337
	$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15
	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	−0.126
	$Sn^{2+} + 2e^- = Sn$	−0.136
	$Ni^{2+} + 2e^- = Ni$	−0.250
	$Co^{2+} + 2e^- = Co$	−0.277
	$Cd^{2+} + 2e^- = Cd$	−0.403
	$Fe^{2+} + 2e^- = Fe$	−0.440
	$Cr^{3+} + 3e^- = Cr$	−0.744
	$Zn^{2+} + 2e^- = Zn$	−0.763
	$2H_2O + 2e^- = H_2 + 2OH^-$	−0.828
	$Al^{3+} + 3e^- = Al$	−1.662
	$Mg^{2+} + 2e^- = Mg$	−2.363
	$Na^+ + e^- = Na$	−2.714
Active	$K^+ + e^- = K$	−2.925

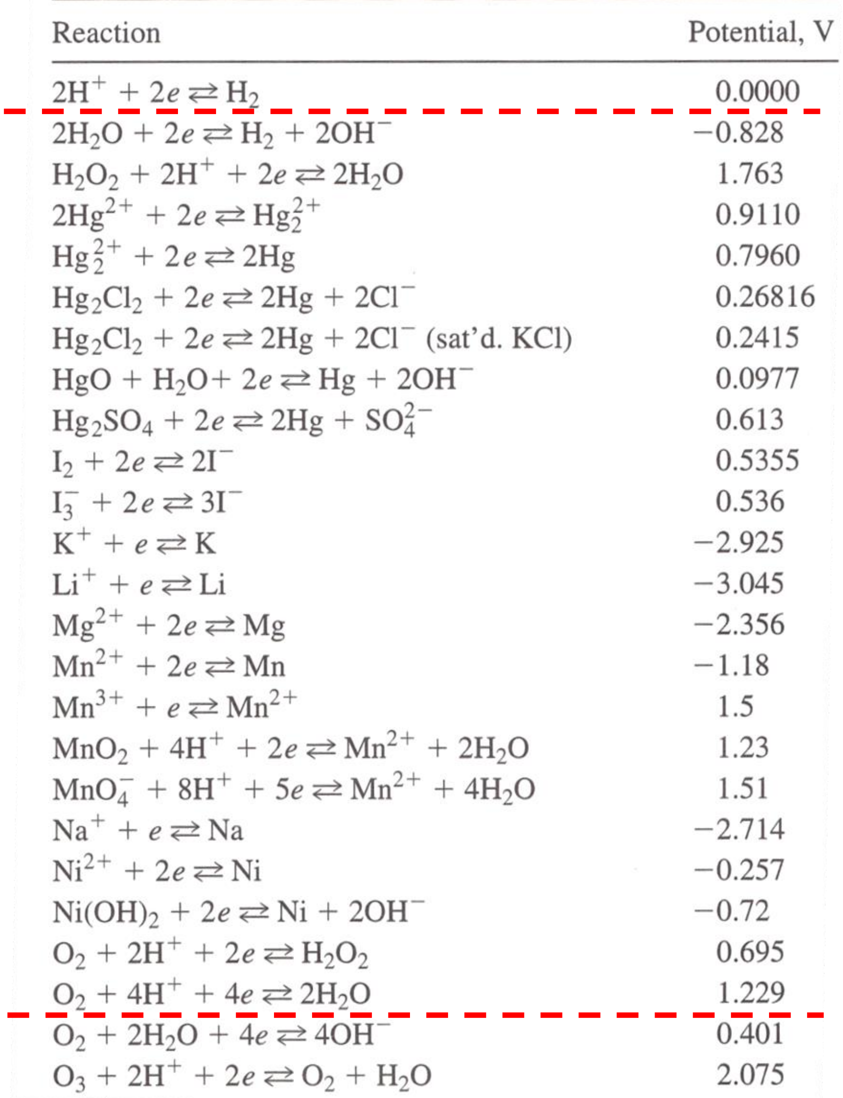
Illustration 2.1

D. A. Jones, Corrosion, Macmillan

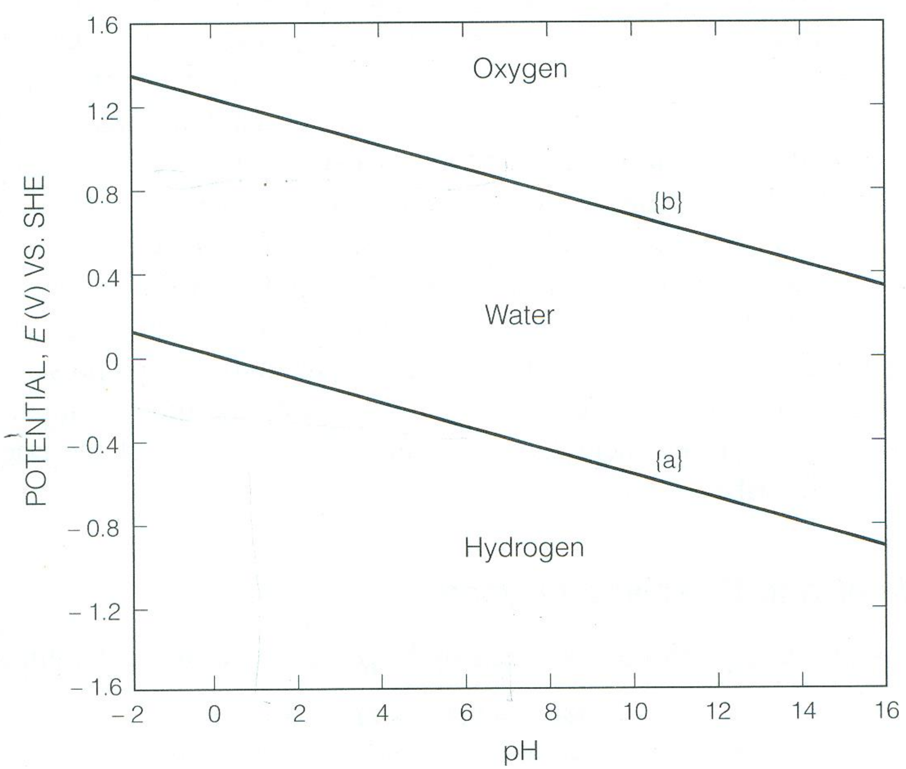
Standard electrode potential (표준전극전위)

E^0

- Standard reduction potential



Reaction	Potential, V
$2H^+ + 2e \rightleftarrows H_2$	0.0000
$2H_2O + 2e \rightleftarrows H_2 + 2OH^-$	−0.828
$H_2O_2 + 2H^+ + 2e \rightleftarrows 2H_2O$	1.763
$2Hg^{2+} + 2e \rightleftarrows Hg_2^{2+}$	0.9110
$Hg_2^{2+} + 2e \rightleftarrows 2Hg$	0.7960
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$	0.26816
$Hg_2Cl_2 + 2e \rightleftarrows 2Hg + 2Cl^-$ (sat'd. KCl)	0.2415
$HgO + H_2O + 2e \rightleftarrows Hg + 2OH^-$	0.0977
$Hg_2SO_4 + 2e \rightleftarrows 2Hg + SO_4^{2-}$	0.613
$I_2 + 2e \rightleftarrows 2I^-$	0.5355
$I_3^- + 2e \rightleftarrows 3I^-$	0.536
$K^+ + e \rightleftarrows K$	−2.925
$Li^+ + e \rightleftarrows Li$	−3.045
$Mg^{2+} + 2e \rightleftarrows Mg$	−2.356
$Mn^{2+} + 2e \rightleftarrows Mn$	−1.18
$Mn^{3+} + e \rightleftarrows Mn^{2+}$	1.5
$MnO_2 + 4H^+ + 2e \rightleftarrows Mn^{2+} + 2H_2O$	1.23
$MnO_4^- + 8H^+ + 5e \rightleftarrows Mn^{2+} + 4H_2O$	1.51
$Na^+ + e \rightleftarrows Na$	−2.714
$Ni^{2+} + 2e \rightleftarrows Ni$	−0.257
$Ni(OH)_2 + 2e \rightleftarrows Ni + 2OH^-$	−0.72
$O_2 + 2H^+ + 2e \rightleftarrows H_2O_2$	0.695
$O_2 + 4H^+ + 4e \rightleftarrows 2H_2O$	1.229
$O_2 + 2H_2O + 4e \rightleftarrows 4OH^-$	0.401
$O_3 + 2H^+ + 2e \rightleftarrows O_2 + H_2O$	2.075



Standard electrode potential not in Table

Desired reaction: $Cr^{3+} + e^{-} \rightarrow Cr^{2+}$

In Table

$Cr^{3+} + 3e^{-} \rightarrow Cr \quad E_{Cr3+/Cr}{}^{0} = -0.74\ V$

$Cr^{2+} + 2e^{-} \rightarrow Cr \quad E_{Cr2+/Cr}{}^{0} = -0.91\ V$

For $Cr^{3+} + 3e^{-} \rightarrow Cr$, $\Delta G^{0} = -3\mathit{F}E_{Cr3+/Cr}{}^{0}$

For $Cr^{2+} + 2e^{-} \rightarrow Cr$, $\Delta G^{0} = -2\mathit{F}E_{Cr2+/Cr}{}^{0}$

For $Cr^{3+} + e^{-} \rightarrow Cr^{2+}$

$$\begin{aligned}\Delta G_{Cr3+/Cr2+}{}^{0} &= -\mathit{F}E_{Cr3+/Cr2+}{}^{0} \\ &= -3\mathit{F}E_{Cr3+/Cr}{}^{0} - (-2\mathit{F}E_{Cr2+/Cr}{}^{0})\end{aligned}$$

$$\begin{aligned}E_{Cr3+/Cr2+}{}^{0} &= 3E_{Cr3+/Cr}{}^{0} - 2E_{Cr2+/Cr}{}^{0} \\ &= 3(-0.74) - 2(-0.91) = -0.40\ V\end{aligned}$$

Standard electrode potential from thermodynamic data

$$aA + bB \rightarrow cC + dD$$

$$\mathbf{\Delta G = \Delta G_f^{products} - \Delta G_f^{reactants} = -nFE_{cell}}$$

ΔG_f: the Gibbs energy of formation

Illustration 2.2

Effect of temperature on standard potential

Positive E_{rxn} (spontaneous reaction))

$$\Delta G = -nFE_{rxn}$$

When all substances are at unit activity, $\Delta G^0 = -nFE_{rxn}{}^0$

$E_{rxn}{}^0$: standard potential of the cell reaction

$$\Delta S = -(\partial \Delta G/\partial T)_p = nF(\partial E_{rxn}/\partial T)_p$$

$$\Delta H = \Delta G + T\Delta S = nF[T(\partial E_{rxn}/\partial T)_p - E_{rxn}]$$

$$RT\ln K_{rxn} = -\Delta G^0 = nFE_{rxn}$$

$$\Delta C_p = (\partial \Delta H/\partial T)_p$$

Illustration 2.3

Nernst equation: activity correction

Cell potential & concentration

Consider $vH_2 + v_O O \rightarrow v_R R + vH^+$

$$\Delta G = \Delta G^0 + RT\ln(a_R^{vR} a_{H+}^{vH+} / a_O^{vO} a_{H2}^{vH2})$$

a: activity ($a_{H+} = a_{H2} = 1$), $\Delta G = -nFE$, $\Delta G^0 = -nFE^0$

Nernst equation

$$E = E^0 - (RT/nF)\ln(a_R^{vR} a_{H+}^{vH+} / a_O^{vO} a_{H2}^{vH2}) = E^0 + (RT/nF)\ln(a_O^{vO}/a_R^{vR})$$

$$E_{rxn} = E_{right} - E_{left} > 0 \text{ (spontaneous reaction)}$$

Formal potential

Activity a = $\gamma[A]$, γ: activity coefficient → unconvenient to use activity due to unknown activity

$$E = E^0 - RT/nF\ \mathit{ln}\ \gamma_R / \gamma_O - RT/nF\ \mathit{ln}\ [R]/[O]$$

$$E = E^{0'} - RT/nF\ \mathit{ln}\ [R]/[O]$$

$E^{0'}$: formal potential

- Ionic strength ⟶ effect on activity coefficient ⟶ formal potential is different from that in each medium → standard potential: from ionic strength to extrapolate to zero ionic strength

Nernst equation (네른스트식)

E obtained from the Nernst equation

$oO + \mathbf{ne^-} = rR$ (reduction)
$pP = qQ + \mathbf{ne^-}$ (oxidation)
$oO + pP = qQ + rR$ E_{cell} (cell reaction)

$$E_{cell} = E^0 - \left(\frac{RT}{nF}\right) \ln \frac{a_Q{}^q a_R{}^r}{a_O{}^o a_P{}^p}$$

a: activity
activity term: minor contribution to the cell voltage

<u>activity</u> (a) → concentration (c); $a = \gamma c$, γ; activity coefficient
$a_i \cong 1$(solvent, pure solid, ideal solution)

Example : $Zn/Zn^{2+}(aq), Cu^{2+}(aq)/Cu$

- **Cell: $Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$**

- Right: $Cu^{2+} + 2e^- \rightarrow Cu \quad E^0 = +0.34$ V
- Left: $Zn^{2+} + 2e^- \rightarrow Zn \quad E^0 = -0.76$ V

$$E_{cell}^{0} = +0.34 - (-0.76) = +1.10 \text{ V}$$

$\Delta G^0 = -2 \times 1.10(V) \times 96485\ (JV^{-1}mol^{-1}) = -212\ kJmol^{-1}$

reaction → spontaneous

$$E_{cell} = E^0 - (RT/2F)\ln(a_{Zn2+}/(a_{Cu2+})$$

If we assume $a_{Zn2+} = a_{Cu2+}$, $E_{cell} = 1.10$ V

Example:

$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$ $\quad E^0 = +\,1.23\ V$

$$E = E^0 + (RT/2F)\ln[(a_{H+}{}^4)/a_{Mn2+}], \quad a_{MnO2}, a_{H2O} = \text{unity}$$

$$\Delta G = -nFE$$

cf. $RT/2F = [(8.314\ JK^{-1}mol^{-1})(298\ K)/2(96485\ JV^{-1}mol^{-1})] = 0.01285\ V$

Illustration 2.4, 2.5

Cell: $PbO_2(s) + Pb(s) + 2H^+(aq) + 2HSO_4^-(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$

From thermodynamics Table,
Standard Gibbs Energy ($kJmol^{-1}$): -813.76 ($PbSO_4(s)$), -237.13 ($H_2O(l)$), -218.96 ($PbO_2(s)$), -755.91 ($HSO_4^-(aq)$), cf) ΔG^0 for element (Pb(s)) and $H^+(aq) = 0$

- **$\Delta G^0 = 2\Delta G^0 (PbSO_4(s)) + 2\Delta G^0 (H_2O(l)) – [\Delta G^0 (PbO_2(s)) + 2\Delta G^0 (HSO_4^-(aq))]$**
  $= -371\ kJmol^{-1}$

➔ $\Delta G^0 = -nFE^0$
➔ $E^0 = 371000(Jmol^{-1})/[2 \times 96485\ (JV^{-1}mol^{-1})] = 1.923\ V$

battery acid: 5.2 M

$$E_{cell} = 1.923\ V – (RT/2F)\ln[a_{H2O(l)}{}^2/(a_{H+(aq)}{}^2 a_{HSO4-(aq)}{}^2)]$$

$$= 1.923\ V – 0.01285\ln[1/(5.2)^2] = 2.008\ V$$

*Calculate cell potential using the reaction below.

$PbO_2 + Pb + 2SO_4^{2-} + 4H^+ \rightarrow 2PbSO_4 + 2H_2O$

Illustration 2.6

Pourbaix diagrams

at 25°C, $pH = -\log_{10}a$

$2H^+ + 2e^- = H_2$

$E = E^0 - (RT/2F)\ln(1/a_{H+}^2)$

$= 0 + (RT/F)\ln(a_{H+})$

$= -(RT/F)(2.303pH)$

$= -0.0592pH$

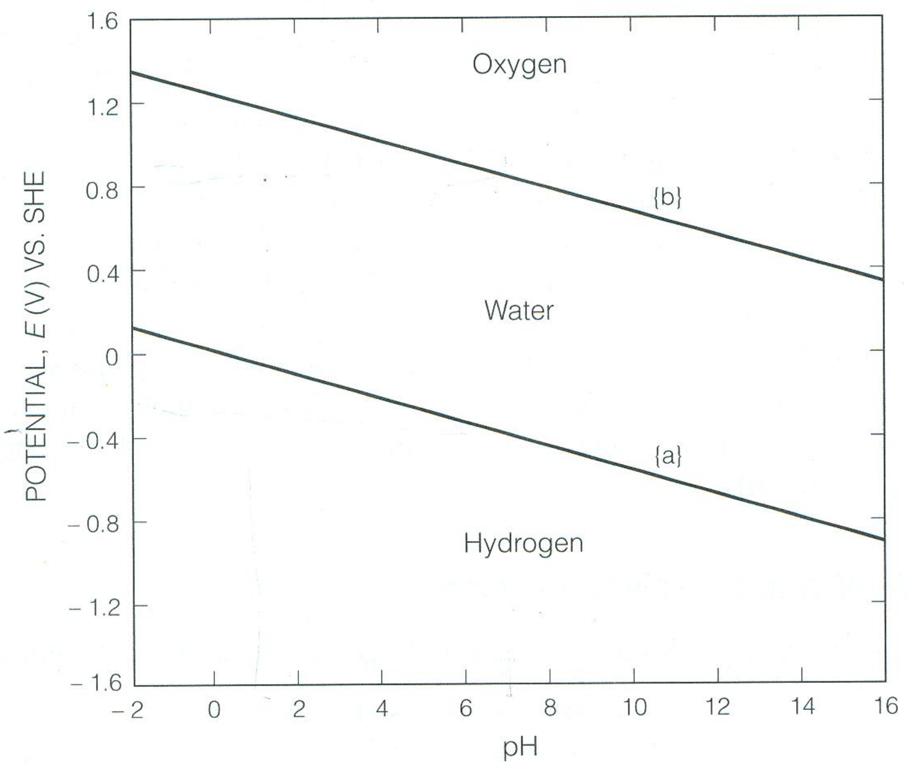
$(1/2)O_2 + 2H^+ + 2e^- = H_2O$

$E = E^0 - (RT/2F)\ln(1/a_{H+}^2)$

$= 1.229 + (RT/F)\ln(a_{H+})$

$= 1.229 - (RT/F)(2.303pH)$

$= 1.229 - 0.0592pH$



Pourbaix diagram for Zn at 25°C

$Zn^{2+} + 2e^{-} = Zn$

$E = E^0 - (RT/2F)\ln(1/a_{Zn2+})$

$= -0.763 + (RT/2F)\ln(a_{Zn2+})$

$[Zn^{2+}] = 10^{-6}$ M → -0.94 V (line c)

$Zn^{2+} + 2OH^{-} = Zn(OH)_2$

No electron transfer reaction (not a function of potential)

→ vertical line (line d)

→ pH calculation using K_{sp}

→ pH = 8.74

$Zn(OH)_2 + 2H^{+} + 2e^{-} = Zn + 2H_2O$

$E = -0.425 - (RT/F)(2.303pH)$

(line e)

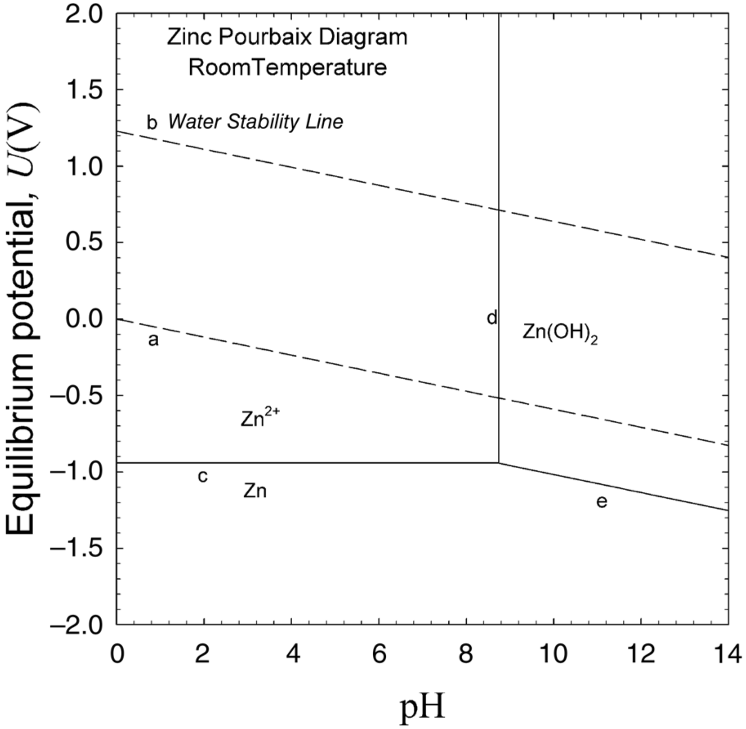


Figure 2.2 Simplified Pourbaix diagram for Zn.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Electrode potential expresses the energy of electrons

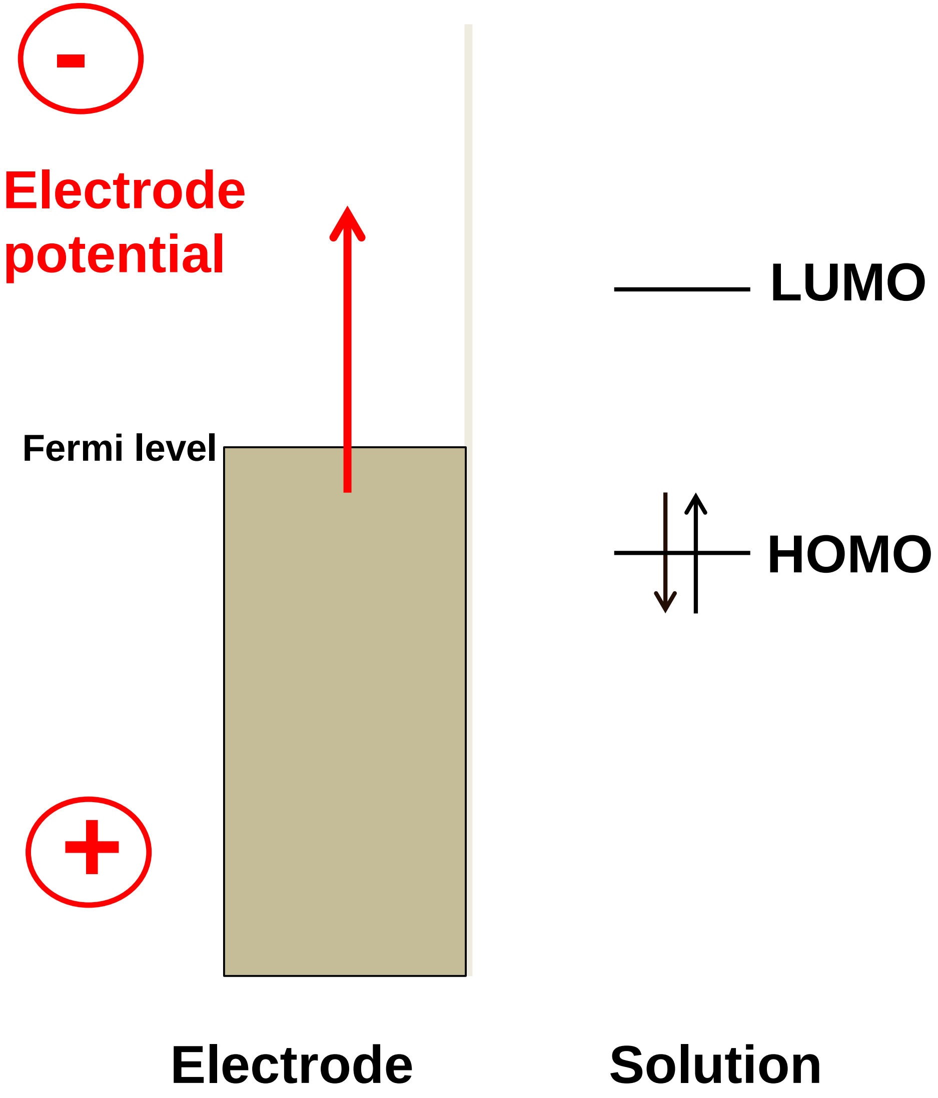
Electrodes

Working electrode(WE): electrode of interest
Reference electrode(RE): second electrode, measure potential of WE with respect to RE
Electrode potential $E = E_{work} - E_{ref}$

Reference electrodes

SHE (standard hydrogen electrode) or NHE(normal hydrogen electrode): universally accepted standard

$$H^+(aq, a=1) + e^- = 1/2H_2(g, 10^5\ Pa) \quad E = 0\ V$$



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Electrode potential

Fermi level

LUMO

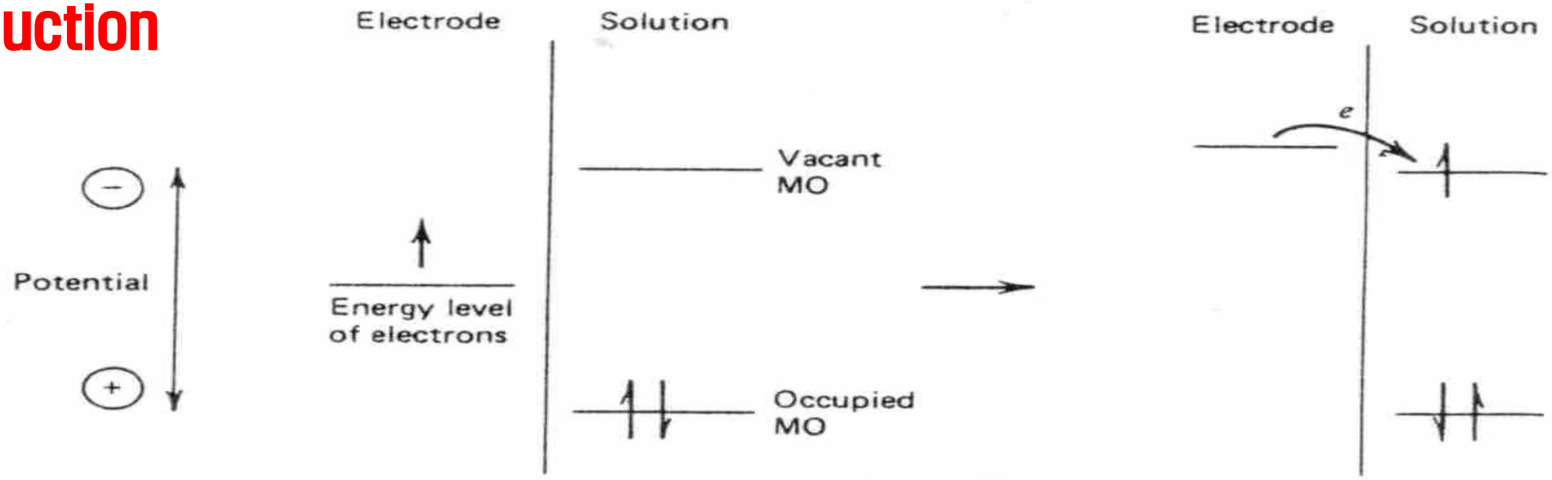
HOMO

+

Electrode

Solution

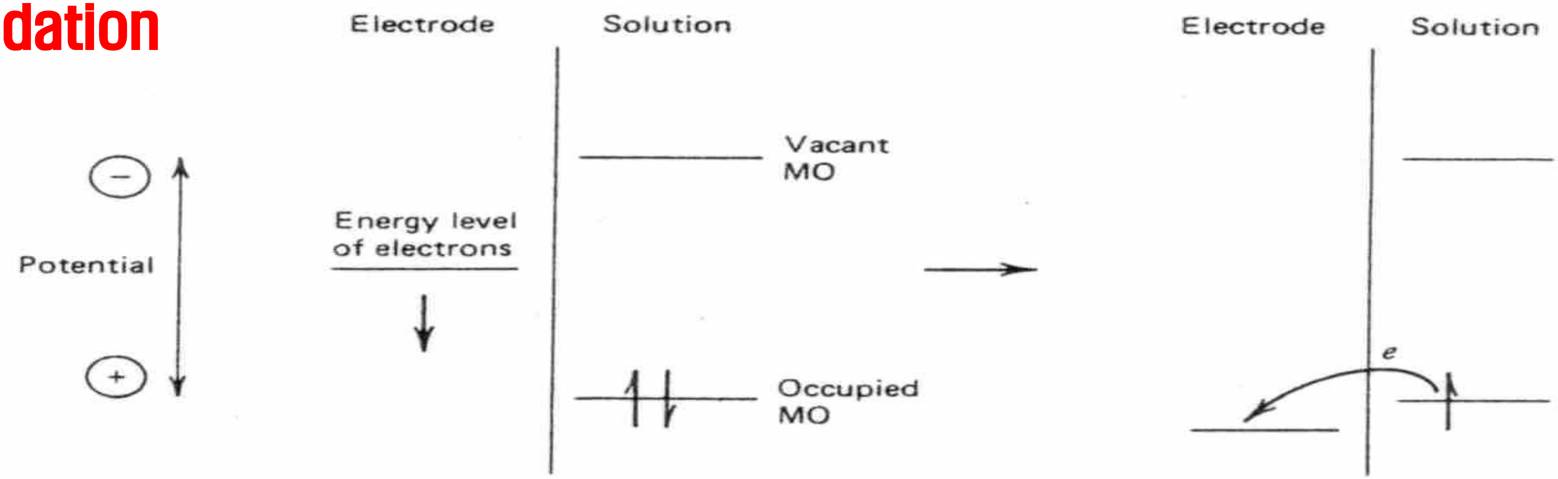
reduction



$A + e \rightarrow A^-$

(a)

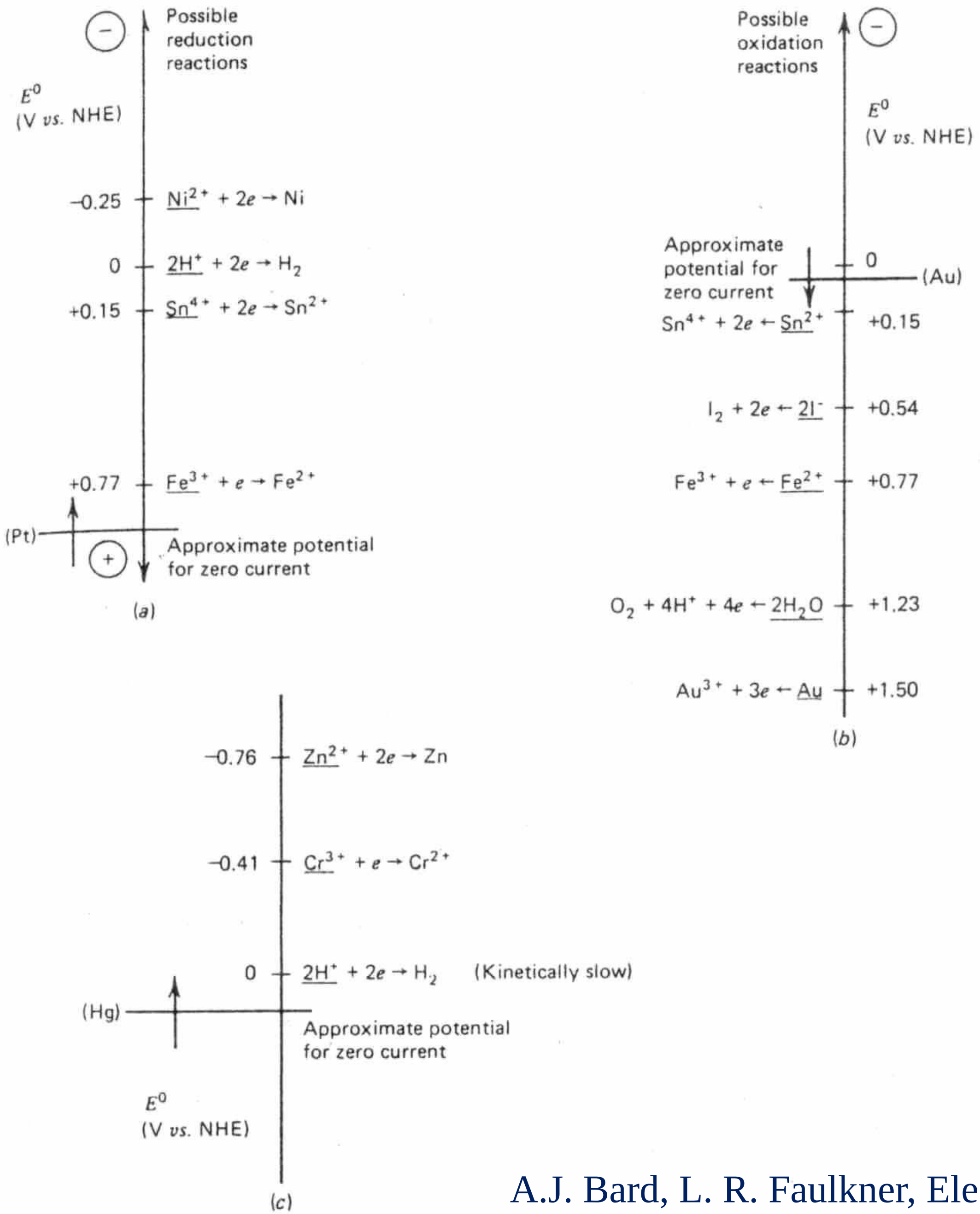
oxidation



$A - e \rightarrow A^+$

(b)

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.



- Potential moved from OCV toward more negative potential: reduced more positive E^0 first
- Potential moved from OCV toward more positive potential: oxidized more negative E^0 first
- consider slow kinetics: slow hydrogen evolution in Hg → Cr^{3+} reduction first in Figure (c)

A.J. Bard, L. R. Faulkner, Electrochemical Methods, Wiley, 2001.

Reference electrode (참조전극)

Electrode potential $E = E_{work} - E_{ref}$

Reference electrodes

SHE (standard hydrogen electrode) or NHE(normal hydrogen electrode): universally accepted standard

$$H^+(aq, a=1) + e^- = 1/2H_2(g, 10^5\ Pa) \quad E = 0\ V$$

SCE (saturated calomel electrode)

$$Hg_2Cl_2(s) + 2e^- = 2Hg + Cl^- \quad E_{ref} = 0.244\ V\ vs.\ NHE$$

Ag/AgCl

$AgCl(s) + e^- = Ag(s) + Cl^-(aq)$ $E_{ref} = 0.199$ V with saturated KCl

Non-Cl system: $Hg/Hg_2SO_4/K_2SO_4$

Nonaqueous system:

- quasireference electrode (QRE):

  Ag or Pt wire in organic solvent (e.g., ferrocene/ferrocenium)

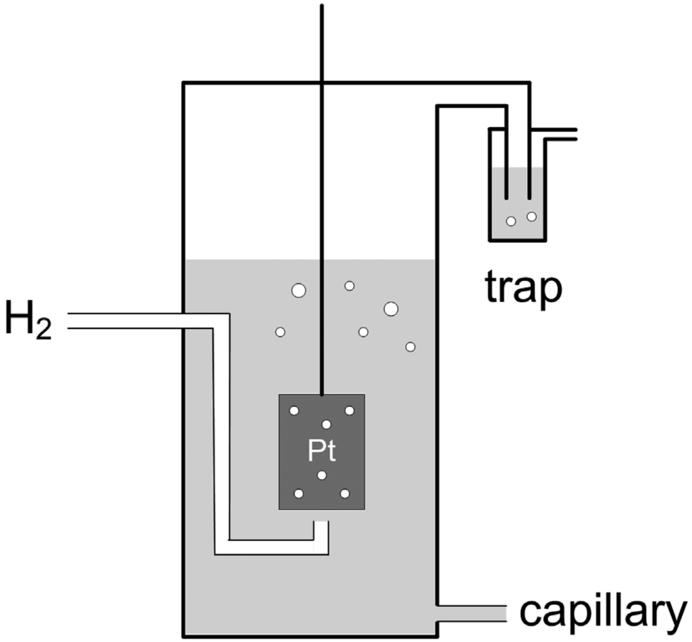


Figure 2.4 Hydrogen reference electrode.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

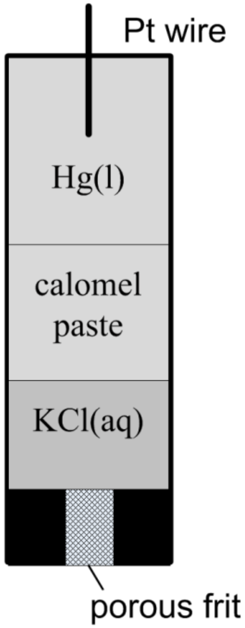


Figure 2.5 Calomel electrode.

Electrochemical Engineering, First Edition. Thomas F. Fuller and John N. Harb.

Companion Website: www.wiley.com/go/fuller/electrochemicalengineering

Reference electrode (참조전극)

Potentials of reference electrodes

E(RHE) = E(NHE) + 0.05916pH

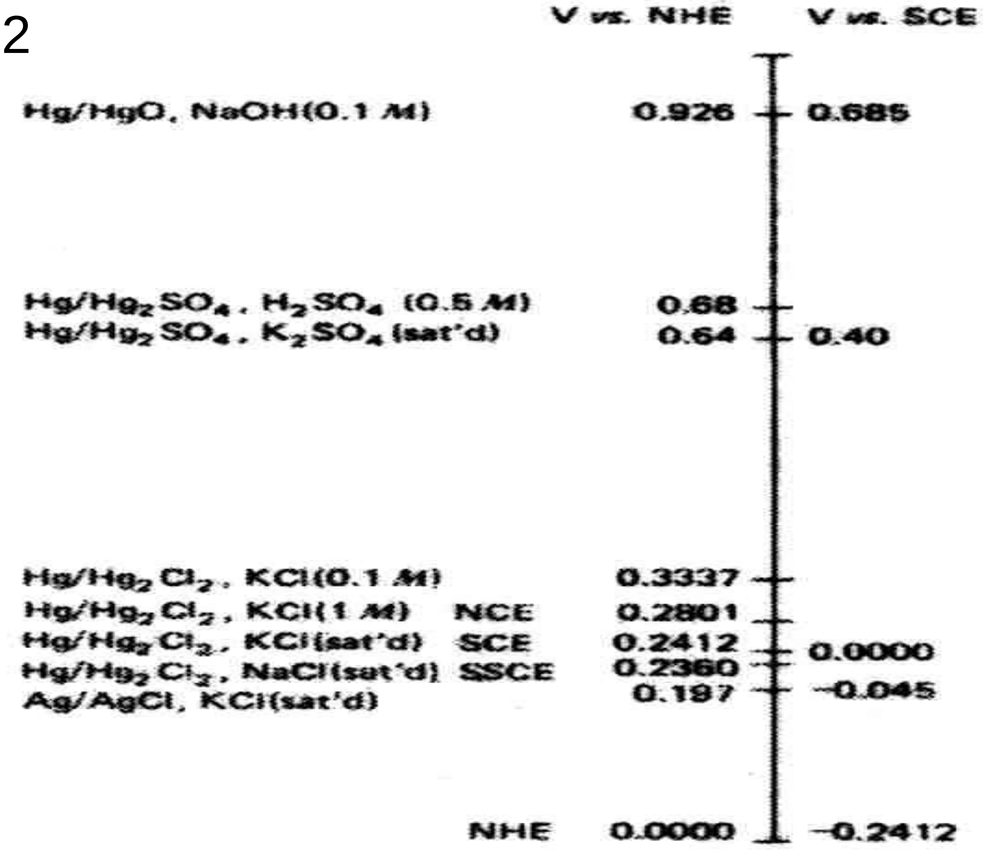
E(SCE) = E(NHE) – 0.2444

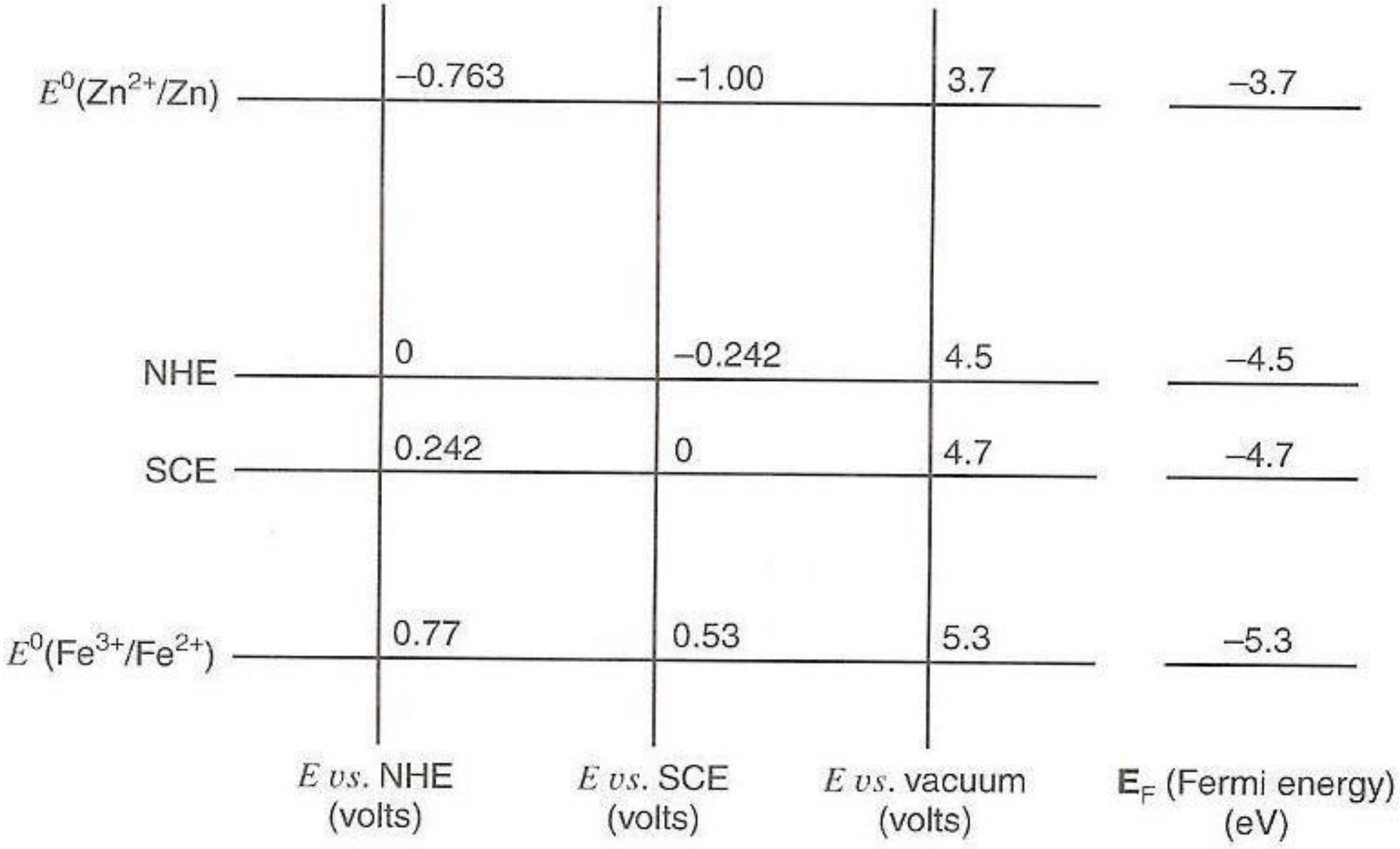
E(Ag/AgCl) = E(NHE) – 0.2223

E(Ag/AgCl, sat.KCl) = E(NHE) – 0.196

E(Hg/HgO 1M KOH) = E(NHE) – 0.1100 + 0.05946pH

E(Hg/Hg_2SO_4) = E(NHE) – 0.6152

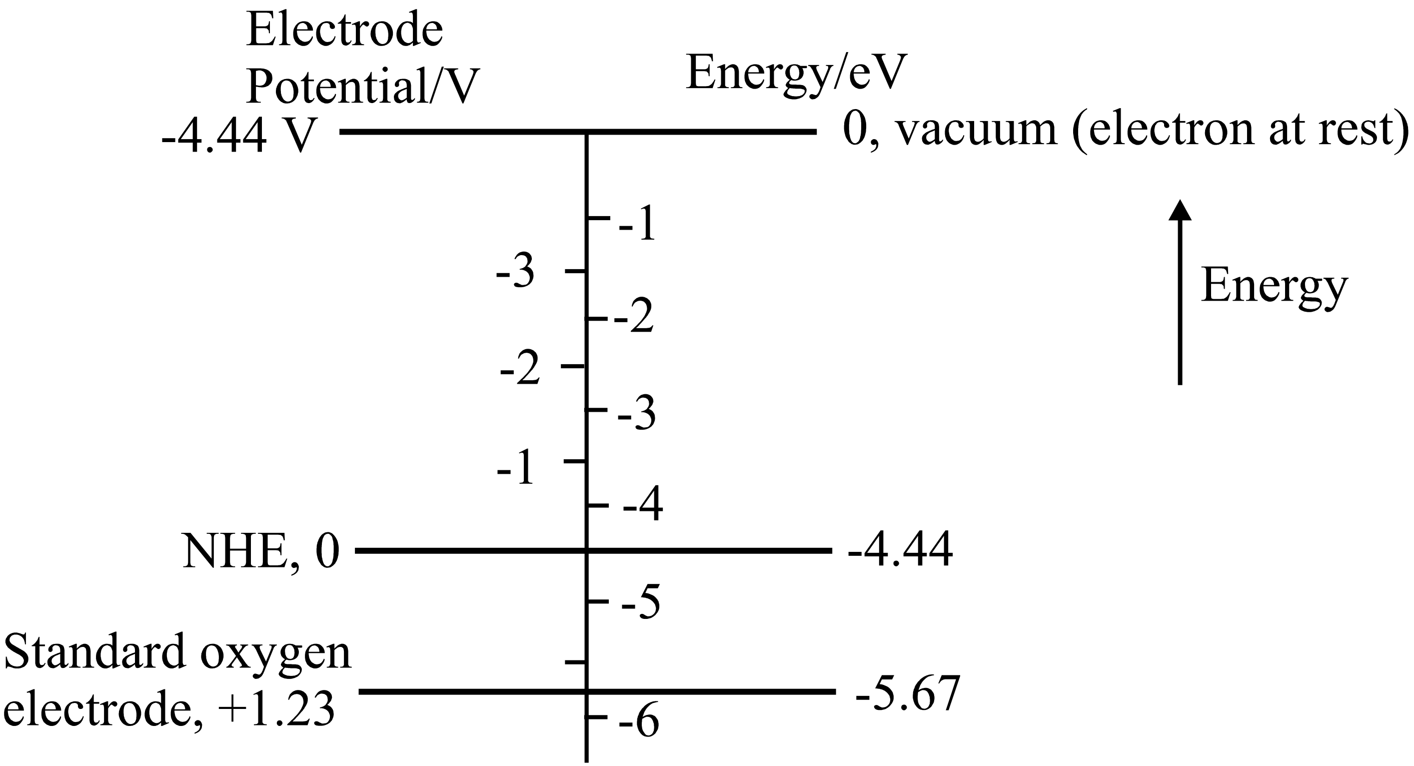




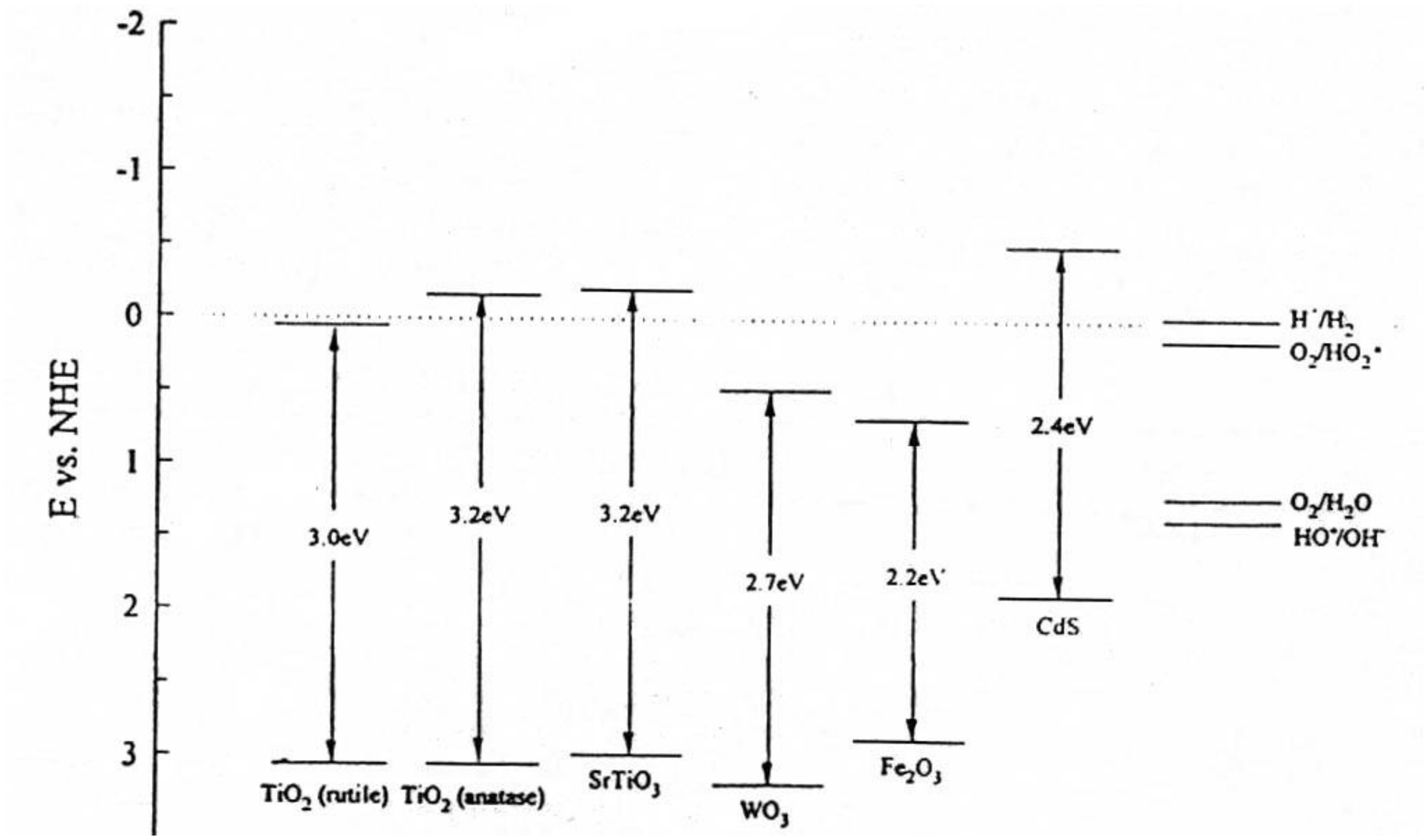
	E *vs.* NHE (volts)	E *vs.* SCE (volts)	E *vs.* vacuum (volts)	$\mathbf{E}_F$ (Fermi energy) (eV)
$E^0(Zn^{2+}/Zn)$	−0.763	−1.00	3.7	−3.7
NHE	0	−0.242	4.5	−4.5
SCE	0.242	0	4.7	−4.7
$E^0(Fe^{3+}/Fe^{2+})$	0.77	0.53	5.3	−5.3

Illustration 2.7

Potential vs. energy (vs. vacuum)



Example: Potential vs. energy (vs. vacuum)



Same way of HOMO, LUMO of organic material or polymer